

SOLID SOLUTION CARBIDES ARE THE KEY FUELS FOR FUTURE NUCLEAR THERMAL PROPULSION

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Abstract

Nuclear thermal propulsion uses nuclear energy to directly heat a propellant (such as liquid hydrogen) to generate thrust for space transportation. In the 1960's, the early Rover/Nuclear Engine for Rocket Propulsion Application (NERVA) program showed very encouraging test results for space nuclear propulsion but, in recent years, fuel research has been dismal. With NASA's renewed interest in long-term space exploration, fuel researchers are now revisiting the Rover/NERVA findings, which indicated several problems with such fuels (such as erosion, chemical reaction of the fuel with propellant, fuel cracking, and cladding issues) that must be addressed. It is also well known that the higher the temperature reached by a propellant, the larger the thrust generated from the same weight of propellant. Better use of fuel and propellant requires development of fuels capable of reaching very high temperatures. Carbides have the highest melting points of any known material. Efforts are underway to develop carbide mixtures and solid solutions that contain uranium carbide, in order to achieve very high fuel temperatures. Binary solid solution carbides (U, Zr)C have proven to be very effective in this regard. Ternary carbides such as (U, Zr, X) carbides (where X represents Nb, Ta, W, and Hf) also hold great promise as fuel material, since the carbide mixtures in solid solution generate a very hard and tough compact material.

This paper highlights past experience with early fuel materials and bi-carbides, technical problems associated with consolidation of the ingredients, and current techniques being developed to consolidate ternary carbides as fuel materials.

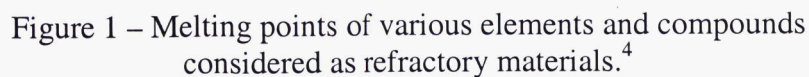
Introduction

Rocket engine performance is measured by the specific impulse or I_{sp} , which is defined as the ratio of thrust to the mass flow rate of the propellant used:

$$I_{sp} = \text{thrust/propellant flow rate} = A \times B \times T/M$$

where A is a performance factor of the propellant, B is a constant that depends on design, T is the core temperature, and M is the molecular weight of the propellant.¹ This equation indicates that rocket performance increases as the engine core temperature increases and propellant molecular weight decreases. Thus a designer may choose hydrogen propellant while simultaneously attempting to increase the engine temperature.

MELTING POINTS OF REFRACTORY MATERIALS



Rover/NERVA Fuels

The Rover/NERVA program used metallic matrices (such as W and Re) as cermet fuels while materials with the highest melting points were used in carbide mixtures (primarily bi- and tri-carbides).⁵ The first set of experiments (named for Rover rockets) used graphite as the base material, due to its high melting point, ease of fabrication, and superior neutronic properties to those of metals. Graphite also acted as a moderator, minimizing the amount of uranium blended for the core. However, graphite sublimated at high temperature, eroded quickly due to its softness, and reacted readily with hydrogen propellant. This erosion also removed fuel particles embedded in the graphite matrix.

During the Rover/NERVA program, as many as 27 rocket engine tests were carried out from 1959 to 1972, allowing new designs to be carried out and advanced fuels to be tested. Total test times increased from 5 minutes to 115 minutes for the final nuclear furnace-1 (NF-1). These efforts facilitated testing of several nuclear engines, as well as very effective development of fuel materials. (See Figure 2.)

Five stages of development were conducted for fuel materials at the Los Alamos Scientific Laboratory (LASL) now known as Los Alamos National Laboratory (LANL). Very early in the program, tests were conducted on UO_2 fuel embedded in graphite, which was readily changed to uranium carbides. Chemical vapor deposition (CVD) was used to coat the carbide particles with ZrC. This protective coating was applied to the carbide fuel kernels, as well as the inside diameter of the hydrogen passage, in order to limit fuel erosion due to the reaction of hydrogen with graphite. Carbon in ZrC has less carbon activity, creating an erosion barrier that made ZrC less susceptible to hydrogen-carbon reaction. However, cracks appeared in the coatings, due to a large difference in thermal expansion between graphite and ZrC. This problem was addressed by developing a composite fuel wherein the graphite matrix existed in a network of U-Zr carbides, reducing the cracking by matching thermal expansion. High coefficient of thermal expansion (CTE) graphites were selected and used, as well.

Towards the end of the Rover/NERVA program, binary carbide fuels of U and Zr carbides were developed to achieve very high temperatures (3000°C) in rocket engines. These fuels prevented any serious loss of carbon, as well as any cracking that would expose the graphite and lead to serious erosion of the fuel. However, the bi-carbide materials received very limited research and testing, leaving much undone.

In 1972, the Rover/NERVA program concluded on an optimistic note concerning carbide fuel elements. Since then, several review reports have been issued and some fuel development efforts undertaken in the U.S. and internationally but, in large part, the advantages of carbide fuels have rarely been tested using a rocket engine. Our understanding of binary carbides – and even tri-carbides – has been furthered by limited research and testing conducted by the Innovative Nuclear Space Power and Propulsion Institute (INSPI) at the University of Florida⁶ and the Russian Scientific Institute (LUTCH) in the former Soviet Union.⁷

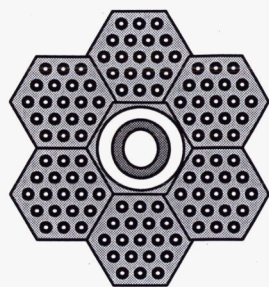
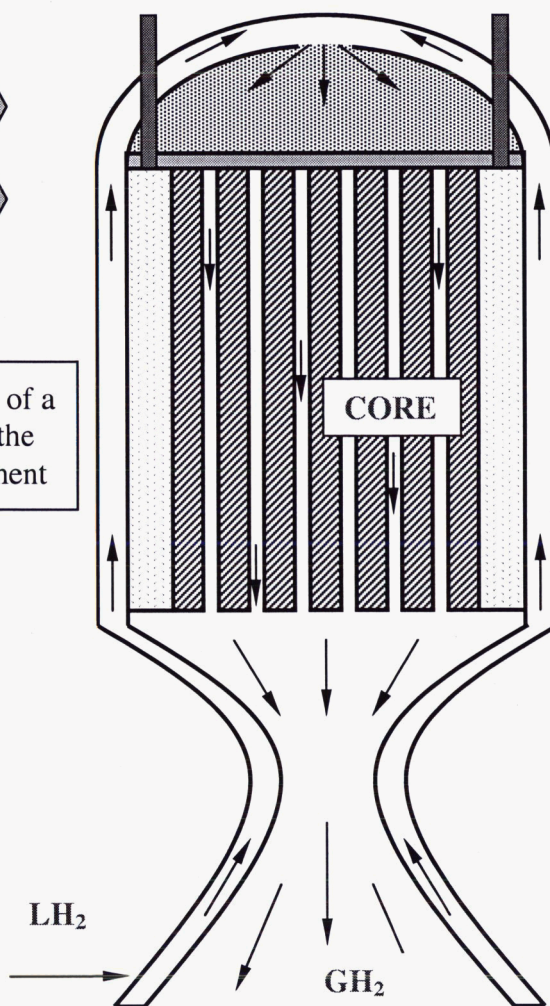


Figure 2 – Schematic of a nuclear engine and the section of a fuel element



Carbide Fuels

Important features have been highlighted for carbide fuels, including their stability in hydrogen. They have very high thermal conductivity compared to conventional oxides (such as UO_2), producing lower thermal gradients between the fuel and propellant that reduce distortion and cracking. Their ability to achieve high operating temperatures will eventually reduce the propellant requirement, allowing more benefit to be reaped from the same volume of liquid hydrogen.

For refractory carbides, the uranium carbides have low melting points (UC at 2525°C , UC_2 at 2480°C) that can be raised by adding other carbides (e.g., ZrC). Certain limitations exist for bi- $[(\text{U}, \text{Zr})\text{C}]$ and tri-carbides $[(\text{U}, \text{Zr}, \text{X})\text{C}]$ where X may be Nb, Ta, or Hf]. Being non-metallic with low ductility, they may crack under the severe thermal cycles typically experienced during the operation of rocket engines. Cracking in solid solution carbides would not cause any harm, since the crack would not expose any graphite-like material for rapid degradation. However, serious problems could occur downstream if the material dislodged after shuddering to pieces. Tests indicated that bi-carbides may develop cracks, while carbide materials do not disintegrate or dislodge.

Processing and shaping can be problematic for these materials, which have very high melting points and are hard to bond using diffusional processes. Most carbides are available in powder form, but the powder technologies available to consolidate them require very high temperatures and pressures, and they may contain voids after processing. These materials are extremely hard and difficult to shape, which means that they require processing with tools that contain diamond tips/wheels.

Processing Carbides

Any material must be shaped by melting, forming, machining, and/or welding in order to produce a component. Here, such processing becomes more difficult due to the reactive nature of carbide materials in atmosphere, their pyrophoricity, angular particle shape, and high hardness. Table 1 lists some relevant physical properties of candidate carbides.⁸ Three consolidation processes – liquid phase sintering, hot pressing, and hot isostatic pressing (HIP)⁹ – are perhaps best suited for this group of materials. They produce much lower porosity levels than the conventional method of binder addition and graphitization.

Table 1 – Important physical properties of carbides for design requirements

Carbide	Melting point (°C)	Crystal structure	Thermal conductivity Cal/cm-sec, C	Co-efficient of thermal expansion X e -6 at 25 °C
Graphite	3652 (subl.)	Hexagonal	0.057	0.6 to 4.3
UC	2525	Cubic	0.057	12.4
UC ₂	2480	Cubic/Tetragonal	0.082	-
ZrC	3423	Cubic	0.049	6.7
TaC	3985	Cubic	0.053	6.3
NbC	3600	Cubic	0.034	6.6
HfC	3950	Cubic	0.015	6.6
WC _{0.6}	2785	Cubic	0.07	5.0 to 4.2

During hot pressing, carbide powder is compressed between a set of graphite dies and punches under pressure while heat is simultaneously applied, with the system placed inside a protective container.¹⁰ Encapsulation in cans followed by high-temperature HIP around 2000 °C is used to obtain excellent consolidation, with porosity levels of less than 1%. (See Figures 3 and 4.) INSPI has successfully employed liquid phase sintering to consolidate tri-carbide materials containing U, Zr and Nb or Ta carbides.⁶ During this process, green compacts are heated to a higher temperature than that of the lowest melting component (generally uranium carbide). The molten carbide fills in porosities while the compacts consolidate by the action of a light force applied in a manner similar to hot pressing. The liquid phase wets the carbide grain boundaries, allowing faster diffusion and homogenization among the carbide phases and leading to a solid solution

product. However, homogeneity, mechanical properties, and microstructural identification remain unexplored for this type of material consolidation process to date.

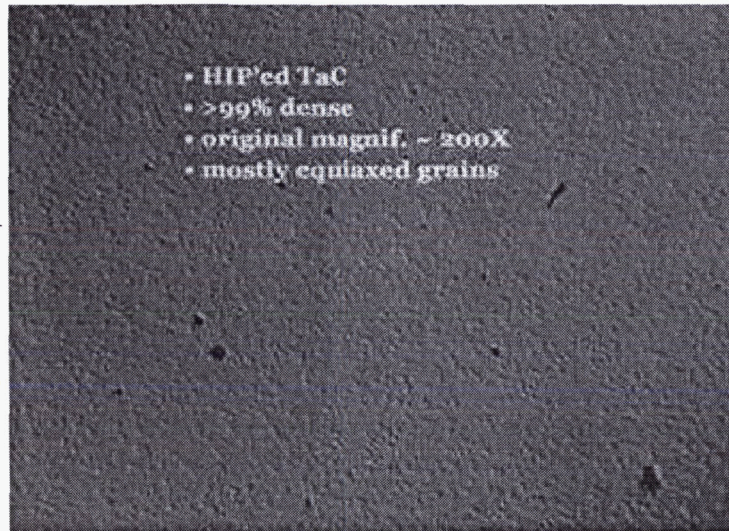


Figure 3 – HIP'ed TaC, as polished. (Courtesy of Exothermics, Inc.)

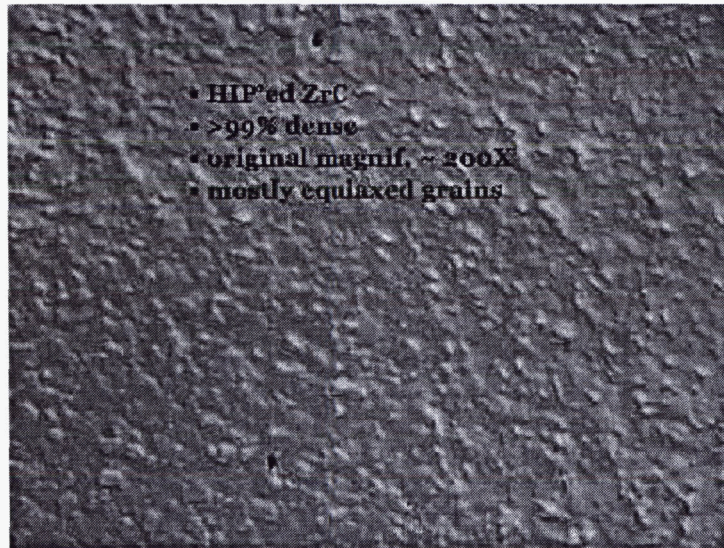


Figure 4 – HIP'ed ZrC, as polished. (Courtesy of Exothermics, Inc.)

Current Efforts

Less severe conditions are required to process multiple carbide mixtures than some of the pure carbides with high melting points (e.g., TaC, ZrC). Evidence exists that modern techniques can fully consolidate these carbides. Therefore, efforts are underway

at NASA's Marshall Space Flight Center to use available high-temperature techniques to consolidate mixed bi- and tri-carbide powders. The initial effort will generate samples in simple shapes (such as a cylinder or a tube) to be tested under extreme temperature and hydrogen pressure conditions that will degrade them. Successful processing and the resultant mechanical and chemical properties will dictate future directions in designing such materials for use as rocket fuels.

Conclusions

1. Thrusters designed with bi- and tri-carbide materials can lead to the generation of high I_{sp} engines.
2. The Rover/NERVA program provided a proving ground that led to the development of solid-solution carbide fuels.
3. Subsequent testing proved the superior properties of carbide materials at various laboratories worldwide.
4. Modern processing can result in low-porosity materials shaped to desired geometries.
5. Subsequent mechanical property evaluation and stability in hydrogen can determine the suitability of these carbide materials for nuclear thermal propulsion applications.

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